Organometallics **1996,** *15,* 1845−1855

Synthesis and Unusual Reactivity of Compounds Containing Silicon−Phosphorus and Silicon−Arsenic Double Bonds: New Silylidenephosphanes and -arsanes of the Type $R_2Si{=}E(SiR_3)$ ($E = P$, As)

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Received November 13, 1995⊗

The monomeric lithium (fluorosilyl)phosphanides $Is_2Si(F)P[LiL_n]R$ (**1**) (Is = 2,4,6-triisopropylphenyl; L = THF, $n = 2, 3$; R = Si*i*Pr$_3$ (**a**), SiMe$_3$ (**b**), Si*t*BuMe$_2$ (**c**), SiPh$_2$Me (**d**), SiPh$_3$ (**e**), Si(Naph)$_3$ (**f**), Si*t*Bu$_2$H (**g**), Ge*t*Bu$_2$H (**h**, L = DME, $n = 1$)) and the related lithium (fluorosilyl)arsanides $Is_2Si(F)As[Li(THF)_2]R$ (**3**) (R = Si*i*Pr$_3$ (**a**), SiPh$_2$Me (**b**), SiCy$_2$Me (**c**, Cy = cyclohexyl)) eliminate LiF and THF (DME) upon heating to give the corresponding silylidenephosphanes and -arsanes **2** and **4**, respectively. The reactivity of the Si=E bonds (E = P (**2a**), As (**4a**)) toward P_4, elemental sulfur, and tellurium is very similar and leads to the corresponding 1,2,3-triphospha-4-silabicyclo[1.1.0]butane (**12**) and to two isomers of arsadiphosphasilabicyclo[1.1.0]butanes, namely 1-(triisopropylsilyl)-4,4-diisityl-1-arsa-2,3-diphospha-4-silabicyclo[1.1.0]butane (**13**) and 3-(triisopropylsilyl)-4,4-diisityl-1-arsa-2,3-diphospha-4-silabicyclo[1.1.0]butane (**14**), respectively. The reaction of S_8 and Te with **2a** gives rise to the corresponding silaphosphathia- and telluracyclopropanes **16** and **17**, respectively. The reaction of **2a** with phenylacetylene yields Is$_2$Si(C≡CPh)PH(Si*i*Pr$_3$) (**18**), and benzonitrile reacts with **2g** and **4c** to give the [2 + 2]-cycloadducts Is$_2$SiE(SiR$_3$)C(Ph)=N (E = P (**19**), E = As (**20**)). Only **4c** reacts with *tert*-butylphosphaacetylene to give Is$_2$SiAs(SiCy$_2$Me)P=C(*t*Bu) (**43**). **2a** reacts with cyclopentadiene to provide the expected hetero Diels−Alder product (**22**). The reaction of **2a** with benzophenone leads to the corresponding 2,1,3-silaphosphaoxetane (**23**), and treatment of **2a** with 1,2-diphenyl-1,2-diketone unexpectedly provides the [2 + 2]-cycloadduct Is$_2$SiP(Si*i*Pr$_3$)C(Ph)(COPh)O (**27**) as the thermodynamic product. The 2,4-di-*tert*-butyl-*o*-quinone solely yields the [2 + 4]-cycloadduct Is$_2$SiP(Si*i*Pr$_3$)O(aryl)O (aryl = 2,4-di-*tert*-butylphenylene) (**31**). The cycloaddition reactions of **2a** and **4a** with diphenyldiazomethane, mesityl azide, and mesityl isocyanide were also investigated, and the respective [2 + *n*]-cycloadducts ($n = 1, 2, 3$) were characterized by means of NMR spectroscopy. For example, **4a** reacts with diphenyldiazomethane to give the [2 + 1]-cycloadduct Is$_2$SiAs(Si*i*Pr$_3$)NN=CPh$_2$ (**29**). The structures of **1h**, **20**, **23**, and **29** were determined by X-ray crystallography.

Introduction

Silicon compounds bearing low coordinated silicon and Si=E bonds (E = main group element), which are stable at room temperature, are convenient and valuable synthetic building blocks in silicon−heteroatom chemistry. This has been widely demonstrated by the use of disilenes (Si=Si),[1] silenes (Si=C)[2] and silanimines (Si=N)[3] as starting materials for the syntheses of several new classes of sila-heterocycles. Although stable phosphasilenes (Si=P) with sterically demanding organyl groups at silicon and phosphorus (type **I**) (Chart 1) have been known since 1984,[4] their isolation, and therefore the study of reactivity, have proven to be very difficult until recently.

In 1991 we reported on the synthesis of *P*-silyl- and *P*-phosphanyl-substituted silylidenephosphanes (phosphasilenes) **2**, i.e. compounds of type **IIA** and **III**, which are accessible by thermally induced elimination of LiF from corresponding *P*-lithium (fluorosilyl)phosphanides **IV**[5,6] (Scheme 1) and possess a remarkable thermal stability (up to 110 °C). In 1993 the first crystalline phosphasilene **5**,[7] a compound of type **IV**, had been prepared and its structure was established by X-ray

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⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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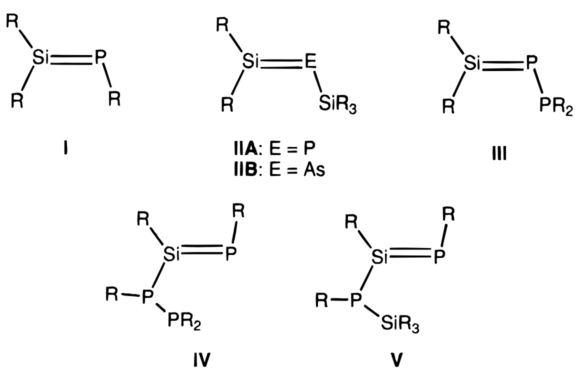
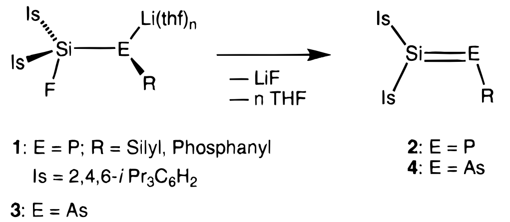
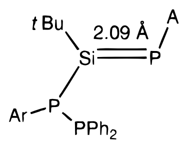
Chart 1



Scheme 1

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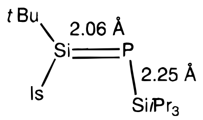
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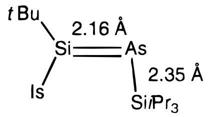
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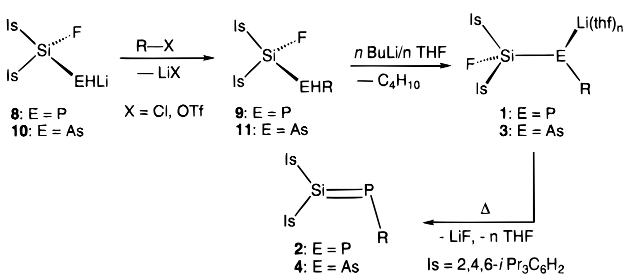
diffraction,[8] whereas the Si=P compounds of type **V** were merely characterized by means of NMR spectroscopy.[9] **5** possesses a relatively long Si=P bond length and a nonplanar geometry around the λ^4,σ^3-Si atom, which can be explained in terms of steric hindrance and/or a second-order Jahn–Teller distortion.[10,11] In comparison, the Si=P bond in **6**[12] is significantly shorter and the Si atom is trigonal planar coordinated.

It has been shown by calculations that the Si–P-π bond in $H_2Si=P(SiH_3)$ is strengthened by hyperconjugation due to the silyl substituent at phosphorus.[13] Furthermore, the stabilizing influence of silyl groups provides that even the Si=As bond in silylidenearsanes (arsasilenes), i.e. compounds of type **IIB**, are surprisingly easy to access. They are similarly formed by thermally initiated elimination of LiF from *As*-lithium (fluorosilyl)arsanides **3**.[12,14] Recently, we performed the structural characterization of compound **7**.[12] Despite the progress in structural investigations of Si=P and Si=As compounds, knowledge of their reactivity is still limited. The thermolability of compounds of types **I**, **IV**, and **V** (stable up to 60 °C) only allowed for reactions with water, methanol, elemental tellurium, and lithium alkanides; these reactions proceed under addition onto the Si=P bond.[4] Further insight into the reactivity of the Si=P bond was provided by trapping experiments of a transient phosphasilene.[15] Because of the conveniently handling of the similar reactive phospha- and arsasilene derivatives **2**, **4**, **6**, and **7**, we have carried out reactions with P_4,[5] elemental Te,[12,14] diphenyldiazomethane,[16] and 1,6-diisocyanohexane,[17] respectively.

Scheme 2



9, 1, 2	a	b	c	d	e	f	g	h
R	$\mathrm{Si^{i}Pr_3}$	$\mathrm{SiMe_3}$	$\mathrm{Si^{t}BuMe_2}$	$\mathrm{SiPh_2Me}$	$\mathrm{SiPh_3}$	Si(Naph)$_3$	$\mathrm{Si^{t}Bu_2H}$	$\mathrm{Ge^{t}Bu_2H}$
n	2	3	3	3	3	3	2	dme

11, 3, 4	a	b	c	
R	$\mathrm{Si^{i}Pr_3}$	$\mathrm{SiPh_2Me}$	$\mathrm{SiCy_2Me}$	Cy = cyclohexyl
n	2	3	3	

In this paper, we report an expanded study of syntheses, spectroscopic characterization, and reactivity of silylidenephosphanes and -arsanes **2** and **4**, which includes the description of the first *P*-germyl-substituted silylidenephosphane (phosphasilene).

Results and Discussion

Syntheses and Structures of Suitable Lithium (Fluorosilyl)pnictides as Starting Materials for Phosphasilenes and Arsasilenes. The syntheses of the phosphasilenes **2a–h** and of the arsasilenes **4a–c** are achieved via the corresponding lithium (fluorosilyl)pnictides **1a–h** and **3a–c**, respectively. It has been shown that perfect steric protection of the highly reactive Si=E bonds (E = P, As) in **2** and **4** is provided by the 2,4,6-triisopropylphenyl substituent (Is = isityl) attached to the low-coordinated silicon center. The appropriate precursors **1** and **3** were prepared in a multiple-step procedure, starting from **8** and **10**, respectively (Scheme 2). The compounds **8** and **10** are formed by the reaction of Is_2SiF_2 with 2 equiv of $[LiEH_2(dme)]$ (E = P, As; dme = 1,2-dimethoxyethane); they show no tendency to eliminate LiF in THF solutions, surely because of the inherent strength of the Si–F bond. Silylation/germylation of **8** furnished the compounds **9** and **11**, respectively, which subsequently were lithiated on phosphorus and arsenic to yield **1** and **3**, respectively. It appears that the success of the next step from **1** (**3**) to **2** (**4**) is naturally dependent on different factors. However, the following three parameters may regarded as crucial: 1. The reaction temperature for the elimination of LiF should not exceed 80 °C. 2. The concen-

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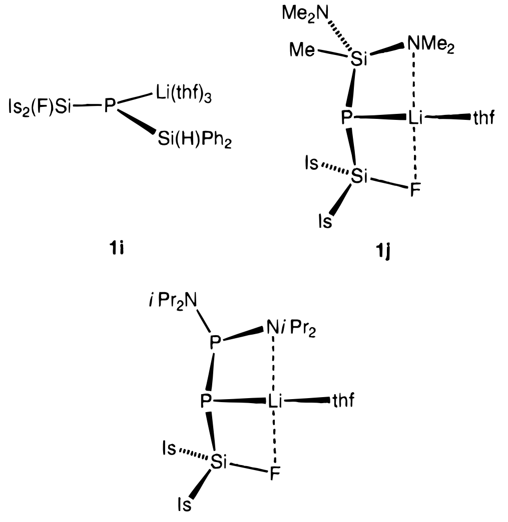
Chart 2



1i **1j** **1k**

tration of **1** (**3**) resolved in hexane or toluene is preferably in the range < 0.1 mol l^{-1}. 3. The steric bulk and electronic influence of the substituent attached to phosphorus should be optimized. In the first instance, the nature of the substituent at phosphorus determines the structures of the precursors **1** and **3**, respectively. This has been demonstrated by a study of a structure–reactivity relationship for several compounds **1**, including the derivatives **1i**–**k** (Chart 2).[6]

The latter investigation revealed that lithium phosphanides **1** are monomeric in solid state and solution, whereby the number x of the donor solvent molecules attached to the lithium center (x = 2, 3) is strongly dependent on the nature of the substituent at phosphorus. It was further observed that phenyl-substituted silyl groups attached to phosphorus in **1i** cause a P(n)/π^* hyperconjugation which essentially seems to stabilize the trigonal-planar geometry around phosphorus and leads to remarkably short Si–P distances (2.16, 2.18 Å). An X-ray structure elucidation of the related phosphanide **1f**, bearing a tri-α-naphthylsilyl group at phosphorus, revealed that the P atom is *not* trigonal-planar surrounded (sum of bond angles at phosphorus 350.4°). Because of the moderate crystal quality of **1f**, however, a discussion of structural parameters is meaningless. Nevertheless, the pyramidal geometry at phosphorus in **1f** suggests that effective hyperconjugative interaction is hampered by steric hindrance from the tri-α-naphthylsilyl group.

Other interesting structural features were observed by a X-ray crystal structure determination of the di-*tert*-butylgermyl-substituted lithium phosphanide **1h** (Figure 1, Table 1).

In this case the lithium center is chelated by one dimethoxyethane (DME) molecule and at the same time attached to the phosphorus and fluorine atoms, as observed in **1j**,**k**. This causes a large pyramidalization on phosphorus (sum of bond angles 268.4°). The Li–F distance is 1.983(6) Å and thus significantly shorter than that observed in **1k** (2.060(8) Å). The Li–F bond seems to be prefered in **1h** for mainly two reasons: the DME ligand is unable to electronically saturate the lithium center and the spatial requirements of the *tert*-butyl groups at germanium force a different conformation of the (F)Si–P(Li) moiety than that observed in **1a**,**b**,**i**.

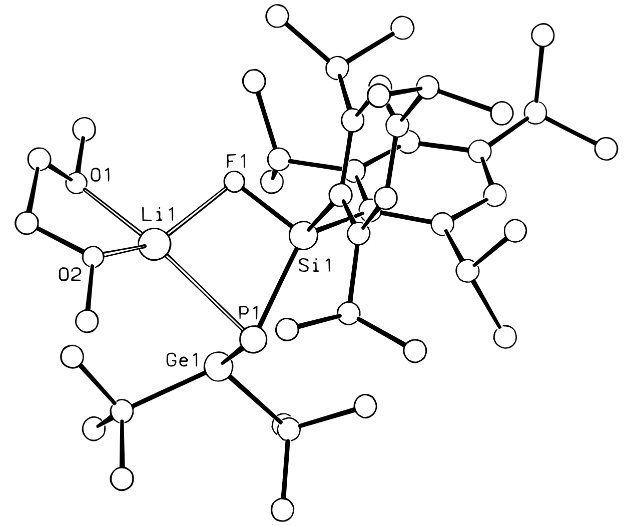


Figure 1. Molecular structure of **1h**. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1h

Ge1–P1	2.301(2)	F1–Li1	1.983(6)
P1–Si1	2.189(2)	O1–Li1	1.979(6)
P1–Li1	2.610(6)	O2–Li1	1.970(6)
Si1–F1	1.678(2)	Ge1–H1	1.52(3)
Si1–P1–Ge1	105.68(6)	P1–Si1–F1	102.17(8)
Li1–P1–Si1	72.1(1)	P1–Si1–C1	117.6(1)
Li1–P1–Ge1	90.6(1)	P1–Li1–F1	81.2(2)
Li1–F1–Si1	101.7(2)	O1–Li1–O2	83.0(1)
F1–Si1–C16	106.0(1)	O1–Li1–F1	98.1(1)

In the case of **1k**, however, the Li–F bond is solely caused by a chelate effect.[6] One methyl hydrogen atom of the *tert*-butyl groups at germanium in **1h** is close by and also contributes to the electronic saturation of the lithium center. This is supported by the relatively short Li–H36 distance of 2.37 Å. Therefore the Li center can be regarded as 5-fold coordinated. The structural features of the arsanides **3** are, as expected, identical with those of the phosphorus analogues **1**.[14]

The derivatives **1a**–**h** exhibit resonance signals in the ^{31}P NMR spectra at characteristically high field, and doublets of doublets, showing relatively large ^1J(Si,P) coupling constants (80–114 Hz), were observed for the ^{29}Si nuclei of the (F)SiP moiety in the ^{29}Si NMR spectra. The ^{29}Si NMR spectroscopic properties of **3a**–**c** are analogous to those observed for **1**. The Li–P bond in the phosphanides **1** does not remain in toluene solution at room temperature. However, a ^{31}P–^{7}Li coupling can be observed in the ^{31}P and ^{7}Li NMR spectrum, respectively, below −70 °C (J = 30–43 Hz), indicating that the structures in solution at low temperature probably resemble those observed in the solid state.

Syntheses and NMR and UV/Vis Spectroscopic Characterization of the Phosphasilenes 2a–h and the Arsasilenes 4a–c. The phosphasilenes **2a**–**h** and the arsasilenes **4a**–**c** were formed by heating solutions of the corresponding derivatives **1a**–**h** and **3a**–**c**, respectively (see Scheme 2). With exception of **2b** (R = $SiMe_3$) and **2e** (R = $SiPh_3$), the Si=P compounds **2** were isolated in the form of yellow or orange-red oils. **2a**–**h** exhibit characteristic ^{31}P and ^{29}Si NMR spectroscopic data which are summarized in Table 2. Noteworthy is the relatively large shielding for the ^{31}P nucleus in the ^{31}P-NMR spectra of **2**, which is quite unusual for

Table 2. ^{29}Si and ^{31}P NMR Data (δ) and Coupling Constants (Hz) of 2a–h (300 K, Solvent C_6D_6)

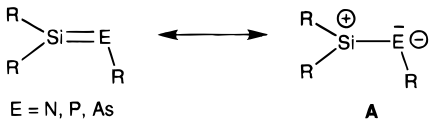
	^{31}P	^{29}Si	^1J(Si=P)	^1J(Si–P)
2a	11.1	167.8 (d, Si=P)	160	
		20.8 (d, Si–P)		78
2b	28.1	172.4 (d, Si=P)	152	
		21.4 (d, Si–P)		75
2c	17.8	178.4 (d, Si=P)	149	
		14.2 (d, Si–P)		72
2d	6.8	180.6 (d, Si=P)	154	
		−3.7 (d, Si–P)		70
2e	3.5	181.7 (d, Si=P)	155	
		−5.0 (d, Si–P)		71
2f	14.4	177.3 (d, Si=P)	158	
		Si–Naph not obsd		
2g	−7.8	179.6 (d, Si=P)	153	
		17.1 (Si–P)		76
2h	4.0	171.9 (d, Si=P)	156	
		–		

compounds bearing two-coordinate phosphorus.[18] Evidently, the latter is caused by the strong σ-donor ability of the silyl and germyl groups, which is also reflected in the comparison of calculated ^{31}P chemical shifts for the parent compounds $H_2Si{=}PH$ (δ = 85) and $H_2Si{=}P(SiH_3)$ (δ = 48).[12,13] In the case of **2g**, the shielding of the phosphorus represents the largest value in this series (δ = −7.8) observed to date. An even more strongly shielded ^{31}P nucleus in phosphasilenes was detected for **6** (δ = −29.9).[12] This unusual finding for **2g** and **6** clearly indicates that steric effects seem to have a considerable influence on the ^{31}P chemical shifts. In line with this, the phosphorus bond angle in **6** (112.7°) significantly exeeds the value calculated for $H_2Si{=}P(SiH_3)$ (100°).[13] In the ^{29}Si NMR spectra the low-coordinate Si atoms reveal doublets at very low field (δ = 167.8–181.7). The ^1J(Si,P) coupling constants (149–160 Hz) are diagnostic for Si–P-π bonds, whereas much smaller values were obtained for saturated silylphosphanes.[18] The resonance signals of the ^{29}Si nuclei of the SiR_3 groups lie in the expected range for saturated silicon compounds; however, the ^1J(Si,P) coupling constants are found to be significantly larger (70–78 Hz) due to the low coordination of the phosphorus. It appears further that all ^{31}P and ^{29}Si chemical shifts are significantly temperature dependent.

The arsasilenes **4a–c** are as thermally resistant as **2**. The low-coordinate Si atom exhibits a singlet at very low field in the ^{29}Si NMR spectrum. The largest deshielding for low-coordinated silicon in arsasilenes known to date has been detected for **7** (δ = 228.8).[12] Remarkably, the Lewis-donor ability of the employed solvent does not significantly affect the ^{29}Si chemical shifts; the same is true for Si=P compounds. This is in contrast to the behavior of silanimines (Si=N)[3] which easily furnish donor solvent adducts. The relatively strong deshielding of the ^{29}Si nuclei in **2** and **4** in comparison to that observed for silanimines is, in the first instance, caused by the smaller HOMO–LUMO gap (π–π*) and probably by a stronger contribution of the polar resonance structure **A** in the electronic ground state (Scheme 3).

(E)/(Z)-isomerization has not yet been observed for both types, phospha- and arsasilenes, and ab initio calculations predict Si=E π bond energies of 34 (E = P) and 30 kcal mol^{-1} (E = As), respectively.[13] We assume that the rotation barrier for the silylated phospha- and arsasilenes **2** and **4** are much lower, since no isomerization was observed on the NMR time scale within the temperature range of −80 to 100 °C. The unusually low barrier could be explained by the presence of sterically demanding substituents.

Scheme 3



A very similar electronic situation of Si=As and Si=P bonds is further reflected by their UV/visible spectra. The λ_{max} values obtained for the Si=P derivatives are as follows: 343 (**2a**, log ε = 2.0), 338 (**2c**, log ε = 2.7), and 331 nm (**2d**, log ε = 2.2). These values probably correspond to n–π* transitions. This assignment is consistent with respective calculated values for electron transitions of $H_2Si{=}P(SiH_3)$. The calculations resulted in values for the n–π* transition of 258 (excitation into the triplet state) and 288 nm (excitation into the singlet state), whereas for the π–π* transition a value of 238 nm was predicted.[13] Blue-shifts of π–π* transitions in comparison to n–π* transitions were also found for phosphaalkenes (P=C).[19] Several superpositions of signals in the region of 200–290 nm (aromatic π system) were observed in the spectra of **2a**,**c**,**d**. Thus the π–π* transitions could not be assigned. However, in the case of arsasilenes both transitions have been observed. Through the expected red-shifts of the n–π* and π–π* transitions we were able to detect both respective transitions in **4a–c**. The λ_{max} values for the n–π* transition were observed at 350 (log ε = 2.3, **4a**), 331 (log ε = 2.2, **4b**), and 346 nm (log ε = 2.2, **4c**), whereas the π–π* transitions were found at 291 (log ε = 1.8, **4a**), 289 (log ε = 2.1, **4b**), and 292 nm (log ε = 1.8, **4c**).

Reactivity of the Phosphasilene 2a and the Arsasilene 4a. The reactivity of the representative derivatives **2a** and **4a** toward P_4, elemental sulfur, tellurium, phenylacetylene, benzonitrile, *tert*-butylphosphaacetylene, and cyclopentadiene (see Scheme 4) and furthermore toward benzophenone, 1,2-diphenyl-1,2-diketone, 3,5-di-*tert*-butyl-*o*-quinone, diphenyldiazomethane, mesityl azide, and mesityl isocyanide was studied (see Scheme 6).

2a and **4a** react with P_4 in the molar ratio of 2:1 to furnish the SiP_3 butterfly-like compound **12** and the $SiAsP_2$ analogous isomers **13** and **14**, respectively. These products are analogous to those observed by the degradation reactions of P_4 and As_4 with disilenes, from which arise Si_2P_2- and Si_2As_2-bicyclo[1.1.0]butanes, respectively.[20,21] The ^{31}P and ^{29}Si NMR spectra indicate that **12** prefers the endo configuration at 25 °C. At higher temperature (>38 °C) the inversion of configuration of the peripheral phosphorus atom is observed in the ^{31}P NMR spectrum and **12** rearranges into the exo isomer **12*** (Scheme 5). For this process a inversion barrier of 23 kcal mol^{-1} has been estimated. Following

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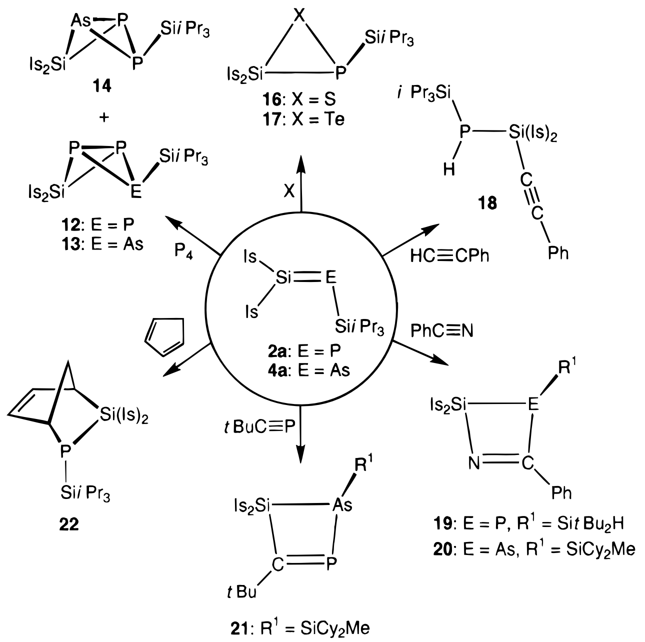
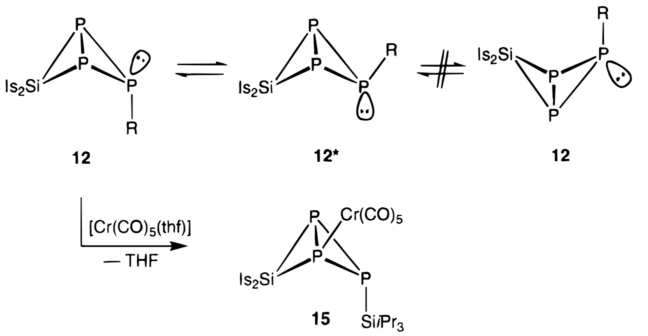
[20] (a) Driess, M.; Fanta, A. D.; Powell, D. R.; West, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1038. (b) Driess, M.; Pritzkow, H.; Reisgys, M. *Chem. Ber.* **1991**, *124*, 1923. (c) Fanta, A. D.; Tan, R. P.; Comerlato, N. M.; Driess, M.; Powell, D. R.; West, R. *Inorg. Chim. Acta* **1992**, *198–200*, 733.

[21] Tan, R. P.; Comerlato, N. M.; Powell, D. R.; West, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1217.

Scheme 4



Scheme 5

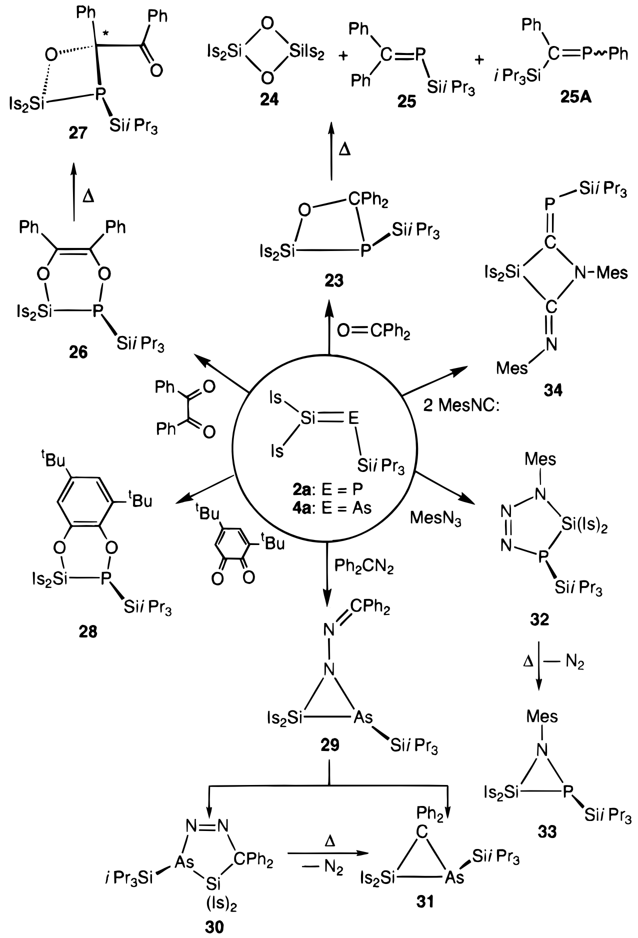


results from MO calculations of P_2Si_2-bicyclo[1.1.0]-butanes,[22] we assume that the SiP_3 system has a very high barrier for ring inversion.

Thus, the temperature dependence of the ^1H, ^{31}P, and ^{29}Si NMR spectra of **12** is probably due to hindered rotation of the bulky aryl rings and phosphorus inversion of the peripheral P atom. The reaction of **4a** with P_4 in the molar ratio 2:1 readily occurs at 40 °C, in which a complicated product mixture was formed. Its ^{31}P NMR spectrum, which could not be completely analyzed, shows multiplet signals in the range of $\delta = 70$ and -260, indicating that a mixture of polycyclic cage compounds occurred. Upon heating of this mixture at 100 °C, the multiplet signals in the ^{31}P NMR spectrum disappeared and the three new signals of **13** and **14** were observed. The approximate ratio of **13** and **14** is 3:2, and they cannot be transformed into each other. The separation of the isomers has not yet been successful.

The reaction of **12** with $[Cr(CO)_5(thf)]$ solely yields the Cr complex **15**, even if the components were mixed in the molar ratio of 1:3 (see Scheme 5). The oxidation of **2a** with elemental sulfur and tellurium quantitatively furnish the three-membered heterocycles **16** and **17**, respectively. The latter do not yield 1,3-dichalcogen-2,4-phosphasilacyclobutanes upon treatment with excess of elemental sulfur and tellurium.

Scheme 6



The Si=E bond in **2a** and **4a**, respectively, turned out to be chemically inert toward dialkyl-, diaryl- and disilyl-substituted alkynes or cyclooctyne at 110 °C. However, if **2a** was stirred with phenylacetylene at 80 °C in toluene, the C−H insertion product **18** was formed. Its structure was determined by means of NMR spectroscopy, mass spectrometry, and a single-crystal X-ray diffraction analysis. However, the moderate crystal quality does not allow a reasonable discussion of structural parameters. The acetylene moiety has added to the Si atom and the phosphorus was protonated, according to the bond polarity of the Si=P bond ($Si^+{-}P^-$). It is interesting to note that the reaction of tetramesityldisilene (Si=Si) with phenylacetylene exclusively yielded the [2 + 2]-cycloaddition product 1,1,2,2-tetramesityl-3-phenyl-disilacyclobut-3-ene.[23] Experiments to convert **18** into the corresponding cyclic silaphosphaheterocyclobut-3-ene, by means of AIBN (azodiisobutyronitrile) as a radical starter for hydrophosphinations, have failed. The Si=E bond in **2a** and **4a** reacts with the strongly polarized C−N triple bond in mesityl cyanide at 25 °C to furnish the [2 + 2]-cycloaddition products **19** and **20**, respectively. The molecular structure of **20** was established by a single-crystal X-ray diffraction analysis (Figure 2, Table 3).

The four-membered SiNAsC framework is slightly puckered (folding angle N−Si−C/Si−C−As 7°), and the As−Si distances are slightly longer than the respective values observed in the four-membered SiOAsC skeleton in a 1,2-silaarsaoxetane derivative.[14] However, the

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(22) Driess, M.; Janoschek, R.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 460.

(23) Young, D. J. D.; West, R. *Chem. Lett.* **1986**, *6*, 883.

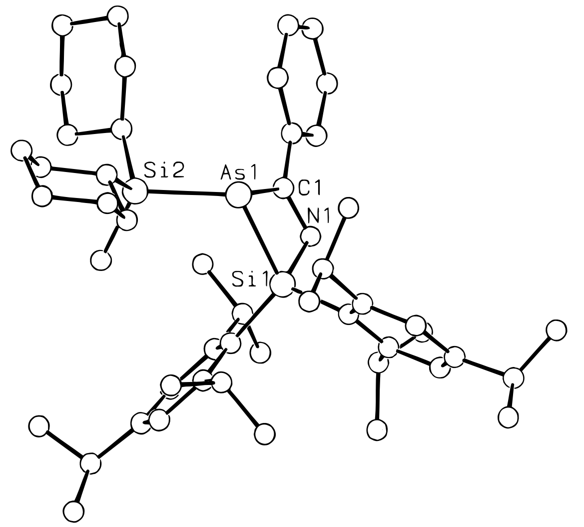

Figure 2. Molecular structure of **20**. H atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 20

As1−C1	1.988(6)	Si1−N1	1.770(5)
As1−Si2	2.397(2)	N1−C1	1.291(7)
As1−Si1	2.402(2)		
C1−As1−Si2	110.0(2)	N1−Si1−As1	80.9(2)
C1−As1−Si1	65.1(2)	C1−N1−Si1	101.4(4)
Si2−As1−Si1	112.72(7)	N1−C1−As1	112.1(4)

As−C bond length (1.988(6) Å) and the endocyclic arsenic bond angle (65.1(2)°) are significantly smaller than the respective values in the latter compound. Evidently, the short C1−N1 distance (1.291(7) Å) in **20** forces a relatively small endocyclic bond angle at silicon. The different bond lengths in the four-membered ring are responsible for distinctly smaller inner angles in comparison to the ideal value of 120° at carbon and nitrogen (112.1(4) and 101.4(4)°), respectively. Analogous adducts which were generated by the reaction of organo cyanides and disilenes are also known.[24b] Surprisingly, the even more reactive C−P triple bond in *tert*-butylphosphaacetylene does not react with the Si═P bond but instead with the Si═As bond in **4c** to furnish the novel heterocycle **21**. According to the reverse polarity of the C−P triple bond compared with the C−N triple bond, the silicon ring atom in **21** is bound to the carbon atom of the C═P moiety. The first [2 + 4]-cycloaddition reaction of the Si═P bond was verified by the reaction of **2a** with cyclopentadiene, which leads to **22**. Interestingly, a Brønsted acid (C−H)−base (Si═P) reaction, as in case of the reaction of **2a** with phenylacetylene, was not observed.

The Si═P bond in **2a** readily reacts like **4a**[14] with benzophenone at −80 °C to form the heterocyclobutane **23** (Scheme 6). The molecular structure of **23** was established by an X-ray structure analysis (Figure 3, Table 4).

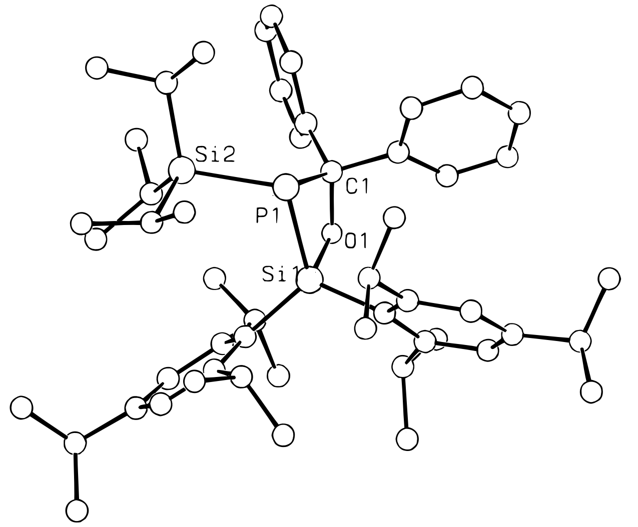

Figure 3. Molecular structure of **23**. H atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 23

P1−C1	1.935(5)	Si1−O1	1.687(3)
P1−Si1	2.281(2)	O1−C1	1.454(5)
P1−Si2	2.296(2)		
C1−P1−Si1	71.0(1)	O1−Si1−P1	82.0(1)
C1−P1−Si2	111.3(2)	O1−Si1−C34	105.5(2)
Si1−P1−Si2	108.06(7)	C34−Si1−C19	118.5(2)
O1−Si1−C19	112.2(2)	C1−O1−Si1	103.2(2)
		O1−C1−P1	101.5(3)

The compound is isotypic with its arsenic homologue.[14] The four-membered SiOPC framework is puckered (along the SiC axis of 16.9°) and strongly trapezoidic distorted due to the different bond lengths in the skeleton. A remarkably long P−C distance (1.935(5) Å) is observed, which is caused by steric hindrance, whereas endocyclic P−C bond lengths in 1,3-diphosphacyclobutanes lie in the range of 1.87−1.91 Å.[25] **23** decomposes upon thermolysis at 160 °C in a sila-Wittig-type reaction to furnish the transient silanone $Is_2Si{=}O$, which immediately dimerizes to the 1,3-disila-2,4-dioxetane **24** and the phosphaalkenes **25** and **25A** (Scheme 6). 1,3-Disila-2,4-dioxetanes are well-known from the work of West et al.[26] Because of the drastic reaction conditions, the expected phosphaalkene **25** partially isomerizes under phenyl and silyl group migration to **25A**. However, such an isomerization process was previously unknown for phosphaalkenes.

If **2a** was allowed to react with PhC(O)−C(O)Ph at 25 °C, surprisingly, the [2 + 4]-cycloadduct **26** was formed in only 10% yield (see Scheme 6). Interestingly, the unexpected [2 + 2]-cycloadduct **27** has been isolated in diastereomerically pure form as the major product. The silyl group at phosphorus in **27** has the *trans*-position relative to the orientation of the phenyl group attached to the chiral carbon center. This has been proven by means of ^{1}H NMR NOESY experiments. On heating, **26** completely rearranges to **27**; that is, **27** is the thermodynamic product. We assume that the higher stability of **27** is due to ring strain in the six-membered C_2O_2SiP skeleton. This enone−ketone isomerization process is unexpected since a relatively strong P−O bond is broken. However, the decrease of ring strain and the formation of the C−O π and P−C σ bonds in **27** may provide an plausible explanation. The

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(24) (a) Weidenbruch, M.; Hamann, J.; Diel, H.; Lentz, D.; von Schnering, H. G.; Peters, K. *J. Organomet. Chem.* **1992**, *426*, 35. (b) Weidenbruch, M. Novel Ring Systems from Cyclotrisilanes and Cyclotristannanes. In *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Studies in Inorganic Chemistry, Vol. 14; Elsevier: Amsterdam, 1992; p 51.

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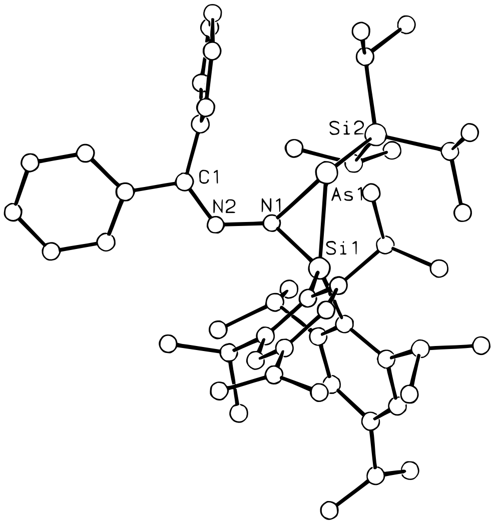

Figure 4. Molecular structure of **29**. H atoms are omitted for clarity.

formation of the four-membered CPSiO framework as in **27** can be prevented if **2a** is treated with 4,6-di-*tert*-butyl-*o*-quinone to furnish the thermally resistent benzo-condensed heterocycle **28** (see Scheme 6). The ^{31}P chemical shift in the ^{31}P NMR spectrum (114.3 ppm) is almost identical with the value observed for **26** (116.3 ppm).

A [2 + 1]-cycloaddition process between the Si=As bond in **4a** and diphenyldiazomethane has been observed. During the addition of Ph_2CN_2 to a solution of **4a** in toluene at −78 °C, the intensive purple color of the diazomethane immediately disappeared. From this reaction mixture the yellow, crystalline [2 + 1]-cycloadduct **29** was isolated, and its molecular structure was established by a X-ray structure analysis (Figure 4, Table 5).

Compound **29** is isotypic with the analogous phosphorus derivative.[16] In comparison to the Si−As distance in the arsenic analogue of **23** (2.38 Å),[14] the Si1−As1 bond length in **29** is somewhat shorter (2.356(3) Å). The endocyclic angle at arsenic is 45.6(2)° and therefore significantly smaller than the corresponding value at phosphorus observed in its phosphorus analogue (49.2°). **29** rearrranges in toluene if heated at 90 °C for 2 days to furnish a mixture of the isomeric [2 + 3]-cycloadduct **30** and the arsasilirane **31**. Further thermolysis leads to tetraphenylethene and as yet unidentified products, whereas the analogous phosphorus compound of **31** cleanly rearranges to an unusual benzobicyclic product.[16]

In contrast to the latter reaction described, the Si=P bond in **2a** readily reacts with mesityl azide at −80 °C in toluene to furnish the [2 + 3]-cycloaddition compound **32** as the primary product and **33** (see Scheme 6). **32** completely transforms into **33** upon heating at 40 °C under loss of N_2. The five-membered $SiPN_3$ skeleton in **32** is unambiguously proven by a relatively strong deshielding of the ring Si atom in the ^{29}Si NMR spectrum (δ −16.7) compared to the values of **29** (δ −81.6), disilaaziridines (δ −50 to −54.6),[27] and **33** (δ −64.7), respectively.

The intriguing reactivity of the Si=E bonds (E = P, As) is also shown by the behavior of **2a** toward mesityl isocyanide. During this reaction, 2 equiv of isocyanide was consumed, even if reacted in an equivalent molar ratio, which leads to the unusual heterocycle **34** bearing an exocyclic imino and phosphaalkenylidene group (see Scheme 6); a reaction intermediate could not be detected by NMR spectroscopy. Analogous results were obtained by the reaction of **2a** and **4a** with 1,6-diisocyanohexane[17] and by the analogous reaction of the Si=As bond in **4a** with cyclohexyl isocyanide.[28] These results further indicate that Si=E bonds (E = P, As) react amazingly similar to silenes (Si=C).[29] Interestingly, by the reaction of silenes with isocyanides the isolation of intermediates has been successful. The Si=Si bond in disilenes, however, reacts with 2 equiv of isocyanide in a stepwise process to furnish disilacyclopropanimines[30] and subsequently 1,3-disilacyclobutan-2,4-di-imines.[24] The structure of **34** was proven by NMR and IR spectroscopy, showing particularly diagnostic δ(^{13}C) values for the carbon atoms of the C=N (169.4) and P=C moieties (207.2), respectively, as well as their *J*(C,P) coupling constants. The ^1J(C,P) value lies in the upper range of values hitherto obtained for phosphaalkenes.[18,31] It is clearly reflected by the ^{31}P chemical shift of the P atom in **34** that the P=C bond is stabilized by π delocalization. Its ^{31}P chemical shift is typical for phosphaalkenes bearing at least one α-amino group attached to the sp^2-carbon atom (C=P).[31]

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 29

As1−N1	1.973(8)	Si1−N1	1.714(7)
As1−Si1	2.356(3)	N1−N2	1.373(9)
As1−Si2	2.400(3)	N2−C1	1.302(11)
N1−As1−Si1	45.6(2)	N1−Si1−As1	55.3(3)
N1−As1−Si2	106.5(2)	Si1−N1−As1	79.1(3)
Si1−As1−Si2	110.67(11)	C1−N2−N1	124.4(9)

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using Schlenk techniques. Solvents were distilled from Na/K alloy and saturated with dry nitrogen or argon. The starting compounds Is_2SiF_2, Is(tBu)SiF_2,[32] and [LiEH$_2$(dme)] (E = P, As; dme = 1,2-dimethoxyethane),[33] the silicon−phosphorus compounds Is$_2$Si(F)PHLi (**8**), Is$_2$Si(F)P(SiiPr$_3$)H (**9a**), Is$_2$Si(F)P(SiiPr$_3$)Li(thf)$_2$ (**1a**), Is$_2$Si=P(SiiPr$_3$) (**2a**), Is$_2$Si(F)P(SitBu$_2$Me)H (**9c**), Is$_2$Si(F)P(SitBu$_2$Me)Li(thf)$_2$ (**1c**), Is$_2$Si=P(SitBu$_2$Me) (**2c**), and Is$_2$SiPPP(SiiPr$_3$) (**11a**),[5] and the silicon−arsenic compounds Is$_2$SiFAsHLi (**10**), Is$_2$SiFAs[Li(thf)$_2$](SiiPr$_3$) (**3a**), Is$_2$Si=As(SiiPr$_3$) (**4a**), and Is$_2$SiFAsH(SiiPr$_3$) (**20a**)[14] were prepared according to the literature.

Physical Measurements. ^{1}H NMR (90, 200 MHz), ^{31}P NMR (36, 81 MHz), ^{19}F NMR (89 MHz), and ^{29}Si (37 MHz) NMR spectra were recorded on a Jeol-FX90Q and/or Bruker AC 200 spectrometer. Chemical shifts (δ) are given relative

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Table 6. ^{31}P and ^{19}F NMR Data (δ) of 9a−h in Hexane

	^{31}P	^{19}F
9a	−241.4 (d, ^1J(P,H) = 191 Hz)	−129.7
9b	−243.1 (d, ^1J(P,H) = 192 Hz)	−129.9
9c	−239.0 (d, ^1J(P,H) = 192 Hz)	−122.1
9d	−236.4 (d, ^1J(P,H) = 196 Hz)	−129.7
9e	−210.0 (d, ^1J(P,H) = 194 Hz)	−128.8
9f	−204.2 (d, ^1J(P,H) = 212 Hz)	−130.7
9g	−237.0 (d, ^1J(P,H) = 198 Hz)	−127.7
9h	−237.4 (d, ^1J(P,H) = 190 Hz)	−127.0

to external standards (^{1}H and ^{29}Si, SiMe$_4$; ^{31}P, 85% aq H$_3$PO$_4$; ^{19}F, CFCl$_3$). UV spectra were recorded on a Perkin-Elmer spectrometer, and mass spectra on a Finnigan MAT 8230. All isolated compounds gave C, H, and (N, P, As) analyses consistent with their formulas, or their compositions were confirmed by high-resolution mass spectrometric measurements.

General Procedure for the Syntheses of Is$_2$Si(F)PH(SiR$_3$) (9b,d−f), Is$_2$Si(F)PH(Ge*t*Bu$_2$H) (9g), Is$_2$Si(F)P[Li(thf)$_2$](SiR$_3$) (1b,d−f) and of Is$_2$Si(F)P[Li(dme)](Ge*t*Bu$_2$H) (1g). In a typical reaction to synthesize **9**, a solution of 1.45 g (2.94 mmol) of **8** in THF was treated with the equimolar amounts of organosilyl chloride and bis(*tert*-butyl)chlorogermane, respectively, at 20 °C affording cloudy solutions. After 6 h of stirring at 20 °C the solvent was evaporated off in vacuum and the residue was taken up in hexane and filtered through a GIII frit to remove LiCl. The ^{31}P and ^{19}F NMR spectra of these solutions indicate that the desired products were formed exclusively (see Table 6).

Therefore, these solutions of **9** were used directly without further purification. In a typical reaction to form the compounds **1**, ca. 30 mL of THF was added to a solution of 2.94 mmol of **9** in ca. 50 mL of hexane and the mixture was treated with the equimolar amount of *n*BuLi at −40 °C to afford a clear orange solution. For the synthesis of **1h**, however, DME was used instead of THF. After removal of the solvents under reduced pressure (10^{-2} Torr), the residue was taken up in a little hexane and the desired products were isolated in form of colorless crystals at room temperature or in form of a yellow oil at −80 °C (**1f**). Yields: 68−87%.

1b: ^{1}H NMR (C$_6$D$_6$, 300 K) δ 0.53 (d, 9 H, SiMe$_3$, *J*(P,H) = 3.8 Hz), 1.09−1.38 (br m, 48 H, CH*Me*$_2$, and 12 H from THF), 2.55 (sept, 2 H, *p*-C*H*Me$_2$, *J* = 6.9 Hz), 3.34 (m, 12 H, THF), 3.61 (br, 4 H, *o*-C*H*Me$_2$), 7.03 (s, 4 H, arom H); ^{19}F NMR (C$_6$D$_6$) δ −117.4 (s); ^{31}P NMR (C$_6$D$_6$, 300 K) δ −298.0 (br). Anal. Calcd for C$_{45}$H$_{79}$FLiO$_3$PSi$_2$: C, 69.18; H, 10.19; P, 3.96. Found: C, 69.08; H, 10.15; P, 3.99.

1d: ^{1}H NMR (C$_6$D$_6$, 300 K) δ 0.71 (s, 3 H, SiMe), 1.12−1.41 (br m, 48 H, CH*Me*$_2$, and 12 H from THF), 2.48 (sept, 2 H, *p*-C*H*Me$_2$, *J* = 6.9 Hz), 3.36 (m, 12 H, THF), 3.66 (br, 4 H, *o*-C*H*Me$_2$), 7.00−7.34 (m, 14 H, arom H); ^{19}F NMR (C$_6$D$_6$) δ −118.9 (s); ^{31}P NMR (C$_6$D$_6$, 300 K) δ −300.0 (br). Anal. Calcd for C$_{55}$H$_{83}$FLiO$_3$PSi$_2$: C, 72.89; H, 9.24; P, 3.42. Found: C, 73.00; H, 9.22; P, 3.38.

1e: ^{1}H NMR (C$_6$D$_6$, 300 K) δ 1.13−1.42 (br m, 48 H, CH*Me*$_2$, and 12 H from THF), 2.35 (sept, 2 H, *p*-C*H*Me$_2$, *J* = 6.9 Hz), 3.38 (m, 12 H, THF), 3.69 (br, 4 H, *o*-C*H*Me$_2$), 6.92−7.39 (m, 19 H, arom H); ^{19}F NMR (C$_6$D$_6$) δ −114.8 (s); ^{31}P NMR (C$_6$D$_6$, 300 K) δ −286.0 (br). Anal. Calcd for C$_{60}$H$_{85}$FLiO$_3$PSi$_2$: C, 74.50; H, 8.85; P, 3.20. Found: C, 73.89; H, 8.76; P, 3.31.

1f: ^{19}F NMR (C$_6$D$_6$) δ −123.8 (s); ^{31}P NMR (C$_6$D$_6$, 300 K) δ −267.8 (br). Anal. Calcd for C$_{72}$H$_{91}$FLiO$_3$PSi$_2$: C, 77.37; H, 8.20; P, 2.77. Found: C, 78.00; H, 8.22; P, 2.83.

1g: ^{1}H NMR (C$_6$D$_6$, 300 K) δ 1.15−1.22 (br m, 36 H, CH*Me*$_2$), 1.17 (s, 18 H, *t*Bu), 1.50 (br, 12 H, THF), 2.70 (m, 2 H, *p*-C*H*Me$_2$, *J* = 6.9 Hz), 3.50 (br m, 16 H, THF and *o*-C*H*Me$_2$), 4.37 (s, 1 H, SiH), 6.97 (s, 4 H, arom H); ^{19}F NMR (C$_6$D$_6$) δ −111.4 (d, ^2J(P,F) = 50.8 Hz); ^{31}P NMR (C$_6$D$_6$, 300 K) δ −291.3 (d, ^2J(P,F) = 50.8 Hz). Anal. Calcd for C$_{46}$H$_{81}$FLiO$_2$PSi$_2$: C, 69.18; H, 10.19; P, 3.96. Found: C, 69.08; H, 10.15; P, 3.99.

1h: ^{1}H NMR (C$_6$D$_6$, 300 K) δ 1.17 (s, 24 H, CH*Me*$_2$), 1.21 (s, 12 H, CH*Me*$_2$), 1.34 (s, 18 H, *t*Bu), 2.76 (m, 2 H, *p*-C*H*Me$_2$, *J* = 6.9 Hz), 3.04 (s, 6 H, OMe), 3.08 (br, 4 H, OCH$_2$), 3.80 (br, 4 H, *o*-C*H*Me$_2$), 4.60 (d, 1 H, GeH, ^2J(P,H) = 10 Hz), 7.10 (s, 4H, arom H); ^{19}F NMR (C$_6$D$_6$) δ −110.1 (s); ^{31}P NMR (C$_6$D$_6$, 300 K) δ −281.6 (br). Anal. Calcd for C$_{42}$H$_{75}$FGeLiO$_2$PSi: C, 65.54; H, 9.82; P, 4.02. Found: C, 66.01; H, 9.91; P, 3.99.

Syntheses of the Silylidenephosphanes Is$_2$Si=P(SiR$_3$) (2b,d−g) and Is$_2$Si=P(Ge*t*Bu$_2$H) (2h). **2b** was formed upon heating of a colorless solution of **1b** (1.04 g, 1.33 mmol) in 50 mL of hexane at 60 °C. The reaction was complete after ca. 6 h, but the ^{31}P NMR spectrum showed that **2b** was formed only in approximately 60% yield besides two byproducts as yet unidentified. **2b** could not be isolated in the pure form and was characterized by means of ^{31}P and ^{29}Si NMR spectroscopy and high-resolution mass spectrometry: ^{31}P NMR (C$_6$D$_6$, 300 K) δ 3.5 (s); ^{29}Si NMR (C$_6$D$_6$, 300 K) δ −5.1 (d, Si−P, ^1J(Si,P) = 71 Hz), 181.7 (d, Si=P, ^1J(Si,P) = 155 Hz); HRMS calcd for C$_{33}$H$_{55}$PSi$_2$ *m/z* 538.3565, found *m/z* 538.3562.

2d was formed in a way similar to the procedure for the synthesis of **2b**, starting from 1.35 g (1.42 mmol) **1d**: Yield 930 mg (1.40 mmol, 98.9%), orange solid; fp 53−55 °C; ^{31}P NMR (C$_6$D$_6$, 300 K) δ 6.8 (s); ^{29}Si NMR (C$_6$D$_6$, 300 K) δ −3.7 (d, SiPh, ^1J(Si,P) = 71 Hz), 180.6 (d, Si=P, ^1J(Si,P) = 154 Hz); HRMS calcd for C$_{43}$H$_{59}$PSi$_2$ *m/z* 662.3877, found *m/z* 662.3872.

2e was formed in a way similar to the procedure for the synthesis of **2b**. The desired product could not be isolated in the pure form. Heating of a colorless solution of **1e** (1.11 g, 1.15 mmol) in 30 mL of hexane yielded an orange solution which contains, after the complete reaction time of 6 h, approximately 45% of **2e**. The desired product was characterized by means of ^{29}Si and ^{31}P NMR spectroscopy and HRMS: ^{31}P NMR (C$_6$D$_6$, 300 K) δ 3.5 (s); ^{29}Si NMR (C$_6$D$_6$, 300 K) δ −5.0 (d, SiPh, ^1J(Si,P) = 71 Hz), 181.7 (d, Si=P, ^1J(Si,P) = 155 Hz); HRMS calcd for C$_{48}$H$_{61}$PSi$_2$ *m/z* 724.4155, found *m/z* 724.4148.

2f was formed in a way similar to the procedure for the synthesis of **2d**. The thermolysis of 1.30 g (1.16 mmol) of **1f** in 20 mL of toluene at 90 °C (32 h) afforded **2f** as an orange solid: Yield 831 mg (0.95 mmol, 82%); ^{31}P NMR (C$_6$D$_6$, 300 K) δ 14.4 (s); ^{29}Si NMR (C$_6$D$_6$, 300 K) δ 177.3 (d, Si=P, ^1J(Si,P) = 158 Hz), ^{29}Si(Naph) not observed; EI-MS (*m/z* (%)) 874 (10) [M$^+$], 732 (8) [(M − Naph − Me)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for C$_{60}$H$_{67}$PSi$_2$ *m/z* 874.463 found *m/z* 874.457.

2g was formed in a way similar to the procedure for the synthesis of **2d**. The thermolysis of 710 mg (0.84 mmol) of **1g** in 60 mL of hexane at 70 °C (10 h) afforded the desired product as an orange oil: Yield 480 mg (0.77 mmol, 92%); ^{1}H NMR (C$_6$D$_6$, 300 K) δ 1.09−1.20 (br, 54 H, *t*Bu and CH*Me*$_2$), 2.70 (m, 2 H, *p*-C*H*Me$_2$), 3.60 (br, 2 H, *o*-C*H*Me$_2$), 3.85 (br, 2 H, *o*-C*H*Me$_2$), 4.51 (d, 1 H, SiH, ^2J(H,P) = 3 Hz), 7.11 (s, 4 H, arom H); ^{31}P NMR (C$_6$D$_6$, 300 K) δ −7.8 (d, ^2J(P,H) = 3 Hz); ^{29}Si NMR (C$_6$D$_6$, 300 K) δ 17.1 (dd, SiH, ^1J(Si,H) = 193 Hz, ^1J(Si,P) = 77 Hz), 179.6 (d, Si=P, ^1J(Si,P) = 152 Hz); EI-MS (*m/z* (%)) 608 (8) [M$^+$], 508 (11) [(M − C$_3$H$_7$ − C$_4$H$_9$)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for C$_{38}$H$_{65}$PSi$_2$ *m/z* 608.4345 found *m/z* 608.4340.

2h was formed in a way similar to the procedure for the synthesis of **2d**. The thermolysis of 650 mg (0.84 mmol) of **1h** in 30 mL of toluene at 80 °C (4 h) afforded the desired product in form of a orange oil: Yield 510 mg (0.76 mmol, 90%); ^{1}H NMR (C$_6$D$_6$, 300 K) δ 1.10 (s, 18 H, *t*Bu), 1.15−1.25 (br, 36 H, CH*Me*$_2$), 2.72 (m, 2 H, *p*-C*H*Me$_2$), 3.53 (br, 2 H, *o*-C*H*Me$_2$), 3.90 (br, 2 H, *o*-C*H*Me$_2$), 4.60 (s, 1 H, GeH), 7.13 (s, 4 H, arom H); ^{31}P NMR (C$_6$D$_6$, 300 K) δ 4.0 (s); ^{29}Si NMR (C$_6$D$_6$, 300 K) δ 171.9 (d, Si=P, ^1J(Si,P) = 156 Hz); EI-MS (*m/z* (%)) 654 (10) [M$^+$, ^{74}Ge], 554 (6) [(M − C$_3$H$_7$ − C$_4$H$_9$)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for C$_{38}$H$_{65}$GePSi *m/z* 654.3795 found *m/z* 654.3796.

Syntheses of Is$_2$Si(F)AsH(SiR$_3$) (11b,c) and Is$_2$Si(F)As[Li(thf)$_2$](SiR$_3$) (3b,c). **11b.** A 5.36 g (10 mmol) amount of the lithium (fluorosilyl)arsanide **10** in 50 mL of THF was treated with 2.32 g (10 mmol) of Ph$_2$MeSiCl at 0 °C to yield a colorless solution. After the solution was warmed to room temperature, the solvent was evaporated to dryness in vacuum (10^{-2} Torr) and the residue was taken up in 20 mL of hexane and filtered over a G-III frit. Removal of the solvent afforded 7.26 g (10 mmol, 100%) of **11b** as a colorless oil: ^{1}H NMR (C_6D_6, 300 K) δ 0.34 (s, 3 H, SiMe), 1.17−1.22 (m, 37 H, CH*Me*$_2$ and AsH), 2.91 (br m, 2 H, *p*-C*H*Me$_2$), 3.89 (br, 2 H, *o*-C*H*Me$_2$), 4.10 (br, 2 H, *o*-C*H*Me$_2$), 7.22−7.27 (m, 8 H, arom H), 7.64−7.81 (m, 4 H, arom H); ^{19}F NMR (C_6D_6) δ −120.2 (s); ^{29}Si NMR (C_6D_6, 300 K) δ 1.31 (s, SiMe), 18.20 (d, SiF, ^1J(Si,F) = 351.7 Hz); EI-MS (*m/z* (%)) 726 (8) [M$^+$], 649 (12) [(M − Ph)$^+$], 453 (100) [Is$_2$SiF$^+$]; HRMS calcd for $C_{43}H_{60}AsFSi_2$ *m/z* 726.3538, found *m/z* 726.3534.

11c. This derivative was prepared similar to **11b**, starting from 5.36 g (10 mmol) of **10** and 2.89 g (10 mmol) of Cy$_2$MeSiBr: Yield 7.38 g (10 mmol, 100%); ^{1}H NMR (C_6D_6, 300 K) δ 0.31 (s, 3 H, SiMe), 0.90−1.66 (m, 59 H, C_6H_{11}, AsH and CH*Me*$_2$), 2.88 (br m, 2 H, *p*-C*H*Me$_2$), 3.91 (br, 2 H, *o*-C*H*Me$_2$), 4.08 (br, 2 H, *o*-C*H*Me$_2$), 7.01 (s, 4 H, arom H); ^{19}F NMR (C_6D_6) δ −119.8 (s); ^{29}Si NMR (C_6D_6, 300 K) δ 12.8 (s, SiMeCy$_2$), 18.43 (d, SiF, ^1J(Si,F) = 353.2 Hz); EI-MS (*m/z* (%)) 738 (10) [M$^+$], 655 (15) [(M − C_6H_{11})$^+$], 453 (100) [Is$_2$SiF$^+$]; HRMS calcd for $C_{43}H_{72}AsFSi_2$ *m/z* 738.4498, found *m/z* 738.4492.

3b. A solution of **11b** (7.26 g, 10 mmol) in 10 mL of THF and 30 mL of toluene was treated with 0.64 g (10 mmol) of *n*BuLi (2.5 M solution in hexane) at −30 °C. Subsequently, the mixture was warmed to room temperature within 2 h and the solvent was removed in vacuum (10^{-2} Torr) to dryness. The residue was taken up in 20 mL of hexane, and the product was crystallized at −30 °C: Yield 8.01 g (9.14 mmol, 91.4%), colorless crystals; fp 148−153 °C (dec); ^{1}H NMR (C_6D_6, 300 K) δ 0.27 (s, 3 H, SiMe), 1.14−1.22 (m, 36 H, CH*Me*$_2$), 1.36 (m, 8 H, THF), 2.79 (sept, 2 H, *p*-C*H*Me$_2$, *J*(H,H) = 6.8 Hz), 3.39 (m, 8 H, THF), 3.59 (br, 4 H, *o*-C*H*Me$_2$), 7.22−7.26 (m, 8 H, arom H), 7.61−7.81 (m, 4 H, arom H); ^{19}F NMR (C_6D_6) δ −118.3 (s); ^{29}Si NMR (C_6D_6, 300 K) δ −0.74 (s, SiMe), 22.50 (d, SiF, ^1J(Si,F) = 327.0 Hz). Anal. Calcd for $C_{55}H_{83}AsFLiO_3PSi_2$: C, 69.58; H, 8.81; As, 7.89. Found: C, 70.01; H, 8.84; As, 7.92.

3c. This derivative was prepared similar to **3b**: Yield 7.63 g (8.6 mmol, 86%) of colorless crystals from 7.38 g (10 mmol) of **11c**; fp 120−122 °C (dec); ^{1}H NMR (C_6D_6, 300 K) δ 0.27 (s, 3 H, SiMe), 0.92−1.66 (m, 66 H, C_6H_{11}, THF and CH*Me*$_2$), 2.65 (sept, 2 H, *p*-C*H*Me$_2$, *J*(H,H) = 6.9 Hz), 3.38 (m, 8 H, THF), 3.73 (br, 4 H, *o*-C*H*Me$_2$), 6.98 (s, 4H, arom H); ^{19}F NMR (C_6D_6) δ −117.2 (s); ^{29}Si NMR (C_6D_6, 300 K) δ 14.2 (s, SiMeCy$_2$), 24.7 (d, SiF, ^1J(Si,F) = 328.8 Hz). Anal. Calcd for $C_{55}H_{95}AsFLiO_3PSi_2$: C, 68.71; H, 9.96; As, 7.79. Found: C, 68.81; H, 9.78; As, 7.65.

Syntheses of Is$_2$Si=As(SiPh$_2$Me) (4b) and Is$_2$Si=As(SiCy$_2$Me) (4c). The procedure is similar to that for **4a**. **4b** was isolated in the form of an orange-red oil: Yield 367 mg (0.52 mmol, 100%) from 460 mg (0.52 mmol) of **3b**; ^{1}H NMR (C_6D_6, 300 K) δ 0.36 (s, 3 H, SiMe), 1.32 (br d, 36 H, CH*Me*$_2$), 2.91 (m, 2 H, *p*-C*H*Me$_2$), 4.01 (br, 2 H, *o*-C*H*Me$_2$), 4.18 (br, 2 H, *o*-C*H*Me$_2$), 7.22−7.27 (m, 8 H, arom H), 7.64−7.81 (m, 4 H, arom H); ^{29}Si NMR (C_6D_6, 300 K) δ 8.6 (s, SiMe), 183.6 (s, Si=As). EI-MS (*m/z* (%)) 706 (17) [M$^+$], 649 (14) [(M − Ph)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for $C_{43}H_{59}AsSi_2$ *m/z* 706.3356, found *m/z* 706.3349.

4c: Yield 345 mg (0.48 mmol, 100%) in the form of a orange oil from 426 mg (0.48 mmol) of **3c**; ^{1}H NMR (C_6D_6, 300 K) δ 0.31 (s, 3 H, SiMe), 0.90−1.65 (m, 58 H, C_6H_{11} and CH*Me*$_2$), 3.56 (sept, 2 H, *p*-C*H*Me$_2$, *J*(H,H) = 6.8 Hz), 4.12 (br, 4 H, *o*-C*H*Me$_2$), 7.01 (s, 4 H, arom H); ^{29}Si NMR (C_6D_6, 300 K) δ 16.4 (s, SiMeCy$_2$), 187.0 (s, Si=As); EI-MS (*m/z* (%)) 718 (12) [M$^+$], 633 (10) [(M − C_6H_{11})$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for $C_{43}H_{71}AsSi_2$ *m/z* 718.4434, found *m/z* 718.4431.

Synthesis of $Is_2\overline{\underline{SiP[Cr(CO)_5]P}}P(Si\textit{i}Pr_3)$ (15). A 250 mg (0.36 mmol) amount of **2a** was treated with 278 mg (1 mmol) of [Cr(CO)$_5$(thf)] in THF at 25 °C, and the solution was stirred for 12 h. After removal of the solvent and a small amount of [Cr(CO)$_6$] in vacuum (10^{-2} Torr, 40 °C), the product was isolated in the form of an orange oil: Yield 310 mg (0.35 mmol, 98%); ^{31}P NMR (C_6D_6) δ −341.9 (dd, P$_A$, *J*(P$_A$,P$_B$) = 80 Hz, *J*(P$_A$,P$_C$) = 132.9 Hz), −220.8 (dd, P$_B$, *J*(P$_A$,P$_B$) = 80 Hz, *J*(P$_B$,P$_C$) = 260.2 Hz), −202.6 (dd, P$_C$, *J*(P$_C$,P$_A$) = 132.9 Hz, *J*(P$_C$,P$_B$) = 260.2 Hz); EI-MS (*m/z* (%)) 876 (3) [M$^+$], 820 (12) [(M − 2CO)$^+$], 684 (11) [(M − Cr(CO)$_5$)$^+$], 157 (100) [Si*i*Pr$_3^+$]; HRMS calcd for $C_{44}H_{67}CrO_5P_3Si_2$ *m/z* 876.3125, found *m/z* 876.3122; IR (ν(CO)) 2061 cm^{-1}.

Reactivity of Is$_2$Si=As(Si*i*Pr$_3$) (4a) toward White Phosphorus. A solution of 912 mg (1.37 mmol) of **4a** in 10 mL of toluene was heated in the presence of 8.5 mg (0.68 mmol) of P$_4$ for 12 h at 100 °C. The solvent was removed in vacuum (10^{-2} Torr), and the residue was taken up in 2 mL of pentane. Crystallization at −80 °C afforded a solid of **13** and **14** in the molar ratio of 2.7:1: Yield 729 mg (1 mmol, 73%), yellow solid; ^{31}P NMR (C_6D_6, 300 K) δ −312.5 (s) (**13**), −299.7 (d, ^1J(P,P) = 183 Hz), −231.7 (d, ^1J(P,P) = 183 Hz) (**14**); ^{29}Si NMR (C_6D_6, 300 K) δ 10.0 (t, Si*i*Pr$_3$, ^1J(Si,P) = 34.8 Hz), −44.5 (t, Is$_2$Si, ^1J(Si,P) = 40 Hz) (**13**), 25.5 (dd, Si*i*Pr$_3$, ^1J(Si,P) = 36 Hz, ^2J(Si,P) + ^3J(Si,P) = 14 Hz), −30.2 (dd, Is$_2$Si, ^1J(Si,P) = 52 Hz, ^2J(Si,P) = 12 Hz) (**14**); EI-MS (*m/z* (%)) 728 (32) [M$^+$], 571 (27) [(M − Si*i*Pr$_3$)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for $C_{44}H_{67}AsP_2Si_2$ *m/z* 728.3588, found *m/z* 728.3582.

Syntheses of $Is_2\overline{SiP(Si\textit{i}Pr_3)E}$ [E = S (16), E = Te (17)]. **16.** A 380 mg (0.61 mmol) amount of **2a** in 40 mL of toluene was reacted with 19.5 mg (0.07 mmol) of S$_8$ at room temperature. Removal of the solvent in vacuum (10^{-2} Torr) afforded the product as a pale yellow oil: Yield 399.5 mg (0.61 mmol, 100%); ^{31}P NMR (C_6D_6) δ −192.0 (s); ^{29}Si NMR (C_6D_6) δ −65.8 (d, Is$_2$Si, ^1J(Si,P) = 72 Hz), 15.7 (d, Si*i*Pr$_3$, ^1J(Si,P) = 96 Hz); EI-MS (*m/z* (%)) 654 (22) [M$^+$], 611 (11) [(M − C_3H_7)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for $C_{44}H_{67}PSSi_2$ *m/z* 654.4221, found *m/z* 654.4218.

17 was prepared in a way similar to that for **16**: Yield 457.8 mg (0.61 mmol, 100%) of yellow crystals from 380 mg (0.61 mmol) of **2a**; fp 208−212 °C (dec); ^{31}P NMR (C_6D_6) δ −267.6 (s); ^{29}Si NMR (C_6D_6) δ −66.5 (d, Is$_2$Si, ^1J(Si,P) = 113 Hz), 2.5 (d, Si*i*Pr$_3$, ^1J(Si,P) = 34 Hz); ^{125}Te NMR δ 1124 (d, ^1J(Te,P) = 483 Hz); EI-MS (*m/z* (%)) 752 (12) [M$^+$, ^{130}Te], 709 (8) [(M − C_3H_7)$^+$], 622 (8) [(M − Te)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for $C_{44}H_{67}PSi_2Te$ *m/z* 752.3568, found *m/z* 752.3564.

Synthesis of Is$_2$Si(C≡CPh)PH(Si*i*Pr$_3$) (18). A 212 mg (0.34 mmol) amount of **2a** in 10 mL of toluene was treated with 35 mg (0.34 mmol) of phenylethyne and heated at 80 °C for 3 h. Removal of the solvent in vacuum (10^{-2} Torr) and crystallization from 1 mL of hexane at room temperature afforded a colorless solid: Yield 183 mg (0.25 mmol, 74%); fp 289−300 °C; ^{1}H NMR (C_6D_6, 300 K) δ 1.22 (d, 42 H, SiCH*Me*$_2$ and *o*-CH*Me*$_2$, *J*(H,H) = 6.9 Hz), 1.27 (d, 6 H, *p*-CH*Me*$_2$, *J*(H,H) = 7 Hz), 1.65 (d sept, 3 H, SiC*H*Me$_2$, *J*(H,H) = 6.9 Hz, ^3J(P,H) = 1.3 Hz), 2.77 (sept, 2 H, *p*-C*H*Me$_2$, *J* = 7 Hz), 4.03 (br, 4 H, *o*-C*H*Me$_2$), 7.10 (s, 4 H, arom H), 6.95−7.47 (m, 5 H, Ph), P*H* not observed; ^{13}C{^{1}H} NMR δ 13.67 (d, SiC, *J*(C,P) = 7.7 Hz), 19.65 (s), 24.15 (s), 24.95 (d, SiC*C*, *J*(C,P) = 14 Hz), 34.63 (s), 97.17 (s, Is$_2$SiCC), 109.97 (s, *C*Ph), 122.66 (s), 129.21 (s), 131.48 (s), 133.79 (s), 133.98 (s), 150.18 (s), 154.45 (s); ^{31}P NMR (C_6D_6, 300 K) δ −234.7 (d, ^1J(P,H) = 205 Hz); ^{29}Si NMR (C_6D_6) δ 21.2 (d, Si*i*Pr$_3$, ^1J(Si,P) = 44.9 Hz), −40.5 (d, IsSi, ^1J(Si,P) = 34.1 Hz); EI-MS (*m/z* (%)) 724 (2) [M$^+$], 535 (100) [(M − PH(Si*i*Pr$_3$))$^+$]; HRMS calcd for $C_{47}H_{73}PSi_2$ *m/z* 724.4969, found *m/z* 724.4966.

Synthesis of $Is_2\overline{SiP(Si\textit{t}Bu_2H)C(Ph){=}N}$ (19). A 213 mg (0.34 mmol) of **2g** in 20 mL of toluene was treated with 35 mg (0.34 mmol) of benzonitrile at −78 °C. The yellow solution was allowed to warm to room temperature within 3 h, and subsequently, the solvent was removed to afford a pale yellow solid: Yield 248 mg (0.34 mmol, 100%); fp 221−224 °C (dec); ^{1}H NMR (C_6D_6, 300 K) δ 1.01−1.18 (br, 54 H, *t*Bu and CH*Me*$_2$), 3.22 (m, 2 H, *p*-C*H*Me$_2$), 4.30 (br, 2 H, *o*-C*H*Me$_2$), 4.45 (br, 2 H, *o*-C*H*Me$_2$), 5.05 (s, 1 H, SiH), 6.95 (s, 4 H, arom H), 7.14−

7.36 (m, 5 H, arom H); ^{31}P NMR (C_6D_6, 300 K) δ −25.4 (s); ^{29}Si NMR (C_6D_6, 300 K) δ 15.1 (dd, SiH, ^1J(Si,H) = 198 Hz, ^1J(Si,P) = 5.1 Hz), −0.9 (d, Is$_2$Si, ^1J(Si,P) = 47 Hz); EI-MS (*m/z* (%)) 711 (6) [M$^+$], 591 (5) [(M − C_3H_7 − Ph)$^+$], 435 (100) [Is$_2$SiH$^+$], 77 (100) [Ph$^+$]; HRMS calcd for $C_{45}H_{70}NPSi_2$ *m/z* 711.4765, found *m/z* 711.4764.

Synthesis of Is$_2$SiAs(SiCy$_2$Me)C(Ph)=N (20). A solution of 208 mg (0.29 mmol) of **4c** in 10 mL of toluene was treated with 29.9 mg (0.29 mmol) of benzonitrile at −60 °C. The mixture was allowed to warm to room temperature within 3 h to afford a pale yellow solution. Removal of the solvent in vacuum (10^{-2} Torr) and recrystallization from 2 mL of hexane afforded a colorless solid: Yield 167 mg (0.20 mmol, 69%); fp 254−256 °C; ^{1}H NMR (C_6D_6, 300 K) δ 0.61 (br, 3 H, SiMe), 0.98−1.60 (m, 58 H, C_6H_{11} and CH*Me*$_2$), 2.57 (br, 2 H, *p*-C*H*Me$_2$), 3.67 (br, 2 H, *o*-C*H*Me$_2$), 4.07 (br, 2 H, *o*-C*H*Me$_2$), 6.92, 7.46−7.43 (br, 9 H, arom H); ^{29}Si NMR (C_6D_6, 300 K) δ 14.2 (s, SiMeCy$_2$), −12.7 (s, Is$_2$Si); EI-MS (*m/z* (%)) 821 (3) [M$^+$], 718 (10) [(M − PhCN)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for $C_{44}H_{67}AsNSi_2$ *m/z* 821.4712, found *m/z* 821.4709.

Synthesis of Is$_2$SiAs(SiCy$_2$Me)P=C(*t*Bu) (21). A solution of 250 mg (0.34 mmol) of **4a** in 0.2 mL of *tert*-butylphosphaacetylene was heated in a sealed NMR tube at 120 °C for 2 d. The reaction process was monitored by ^{31}P and ^{29}Si NMR spectroscopy. Removal of volatile components in vacuum (10^{-2} Torr) and recrystallization of the residue from 1 mL of hexane at −80 °C afforded a yellow solid: Yield 105 mg (0.13 mmol, 38%); fp 254−256 °C; ^{1}H NMR (C_6D_6, 300 K) δ 0.71 (br, 3 H, SiMe), 0.98−1.65 (m, 67 H, C_6H_{11}, *t*Bu and CH*Me*$_2$), 2.78 (br, 2 H, *p*-C*H*Me$_2$), 3.99 (br, 2 H, *o*-C*H*Me$_2$), 4.23 (br, 2 H, *o*-C*H*Me$_2$), 6.92 (br, 4 H, arom H); ^{29}Si NMR (C_6D_6, 300 K) δ 16.9 (s, SiMeCy$_2$), 11.8 (d, Is$_2$Si, ^2J(Si,P) = 8 Hz); ^{31}P NMR δ 387 (s); selected ^{13}C{^{1}H} NMR data δ 240.5 (d, C=P, ^1J(C,P) = 82.7 Hz); EI-MS (*m/z* (%)) 818 (1) [M$^+$], 718 (5) [(M − *t*BuCP)$^+$], 435 (100) [Is$_2$SiH$^+$]; HRMS calcd for $C_{48}H_{80}AsPSi_2$ *m/z* 818.4731, found *m/z* 818.4725.

[2 + 4]-Cycloaddition Reaction of 2a with Cyclopentadiene To Form 22. A 200 mg (0.32 mmol) amount of **2a** in 5 mL of toluene was mixed with 21.1 mg of cyclopentadiene and stirred at room temperature for 5 h. Removal of the solvent afforded 221 mg (0.32 mmol, 100%) of the pure product in form of a colorless solid: fp 153−155 °C; ^{1}H NMR (C_6D_6, 300 K) δ 0.38 (d, 3 H, CH*Me*$_2$, *J*(H,H) = 7 Hz), 0.67 (d, 3 H, CH*Me*$_2$, *J*(H,H) = 7 Hz), 1.17−1.67 (m, 51 H, CH*Me*$_2$), 2.34 (d, 1 H, AM-spin system, CH$_2$-bridge, *J*(H,H) = 11.5 Hz), 2.40 (br, 1 H, C*H*Me$_2$), 2.62 (m, 2 H, *p*-C*H*Me$_2$), 3.31 (br, 1 H, C*H*Me$_2$), 3.41 (d, 1 H, CH$_2$-bridge, *J*(H,H) = 11.5 Hz), 3.75 (m, 2 H, C*H*C=C), 5.31 (m, 1 H, *H*C=CH), 5.44 (m, 2 H, C*H*Me$_2$), 6.11 (m, 1 H, HC=C*H*), 6.30 (d, 1 H, arom H, *J*(H,H) = 12.8 Hz), 7.00 (br, 2 H, arom H), 7.13 (d, 1 H, arom H, *J*(H,H) = 12.8 Hz); ^{31}P NMR (C_6D_6, 300 K) δ −153.4 (s); ^{29}Si NMR (C_6D_6) δ 15.1 (d, Si*i*Pr$_3$, ^1J(Si,P) = 71.4 Hz), −4.8 (d, IsSi, ^1J(Si,P) = 31.8 Hz); EI-MS (*m/z* (%)) 688 (8) [M$^+$], 622 (42) [(M − C_5H_6)$^+$], 434 (100) [(Is$_2$SiH − 1)$^+$]; HRMS calcd for $C_{44}H_{73}PSi_2$ *m/z* 688.4969, found *m/z* 688.4960.

Synthesis of Is$_2$SiP(Si*i*Pr$_3$)CPh$_2$O (23). A 340 mg (0.54 mmol) amount of **2a** in 10 mL of toluene was reacted with 98.3 mg (0.54 mmol) of benzophenone at −78 °C. The reaction mixture was warmed to room temperature, and the solvent was removed (10^{-2} Torr), followed by crystallization of the product from 1 mL of hexane at room temperature: Yield 382 mg (0.47 mmol, 88%); fp 148 °C; ^{1}H NMR (C_6D_6, 300 K) δ 0.28 (br, 3 H, CH*Me*$_2$), 0.47 (br, 3 H, CH*Me*$_2$), 1.07−1.58 (m, 51 H, CH*Me*$_2$), 2.73 (sept, 2 H, *p*-C*H*Me$_2$, *J*(H,H) = 6.8 Hz), 3.00 (br, 1 H, *o*-C*H*Me$_2$), 3.59 (br, 1 H, *o*-C*H*Me$_2$), 4.70 (br, 1 H, *o*-C*H*Me$_2$), 4.84 (br, 1 H, *o*-C*H*Me$_2$), 6.75−7.25 (m, 10 H, arom H), 7.73 (s, 2 H, arom H), 7.77 (s, 2 H, arom H); ^{31}P NMR (C_6D_6, 300 K) δ −18.8 (s); ^{29}Si NMR (C_6D_6) δ 16.8 (d, Si*i*Pr$_3$, ^1J(Si,P) = 75 Hz), 8.2 (d, IsSi, ^1J(Si,P) = 4.9 Hz); ^{13}C{^{1}H} (C_6D_6) δ 15.4 (d, Si*C*HMe$_2$, ^2J(C,P) = 8.7 Hz), 20.38 (s), 24.72 (s), 25.65 (s), 27.06 (s), 30.32 (s), 33.20 (s), 34.50 (s), 35.03 (s), 36.09 (s), 88.21 (d, P*C*O, ^1J(C,P) = 23.3 Hz), 121.54 (s), 122.85 (s), 123.89 (s), 125.96 (s), 149.78 (s), 150.77 (s), 154.30 (s), 156.10 (s). EI-MS (*m/z* (%)) 805 (8) [M$^+$], 648 (24) [(M − Si*i*Pr$_3$)$^+$], 623 (100) [(M − OCPh$_2$)$^+$], 433 (96) [(Is$_2$Si − 1H)$^+$]. Anal. Calcd for $C_{52}H_{77}OPSi_2$: C, 77.55; H, 9.63; P, 3.84. Found: C, 77.21; H, 9.62; P, 3.90.

Thermolysis of 23 into Is$_2$SiOSiIs$_2$O (24), Ph$_2$C=P(Si*i*Pr$_3$) (25), and Ph(Si*i*Pr$_3$)C=P(Ph) (25A). Heating of a solution of **23** (300 mg, 0.37 mmol) in toluene at 160 °C for 2 d in a sealed NMR tube afforded a mixture of the three products **24**, **25**, and **25A** which were identified by NMR spectroscopy and mass spectrometry. The recorded ^{29}Si NMR spectroscopic data of **24** are identical with those reported in the literature.[34] Selected ^{13}C{^{1}H} NMR data of **25**: δ 201.0 (d, C=P, ^1J(C,P) = 88 Hz). ^{31}P NMR (C_6D_6): δ 293.7 (s). ^{29}Si NMR: δ 28.4 (d, Si*i*Pr$_3$, ^1J(Si,P) = 63 Hz). EI-MS (*m/z* (%)) 354 (34) [M$^+$], 197 (82) [(M − Si*i*Pr$_3$)$^+$], 43 (100) [$C_3H_7^+$]. Selected ^{13}C{^{1}H} NMR data of **25A**: δ 189.0 (d, C=P, ^1J(C,P) = 67 Hz). ^{31}P NMR (C_6D_6): δ 281.9 (s). ^{29}Si NMR: δ 12.2 (d, Si*i*Pr$_3$, ^2J(Si,P) = 17 Hz). EI-MS (*m/z* (%)) 354 (34) [M$^+$], 280 (41) [(M − Ph)$^+$], 43 (100) [$C_3H_7^+$]. HRMS: calcd for $C_{22}H_{31}PSi$, *m/z* 354.1924, found, *m/z* 354.1918.

Reaction of 2a with PhC(O)C(O)Ph and 1,2,3,5-C$_6$H$_2$(CO)$_2$(*t*Bu)$_2$ To Form Is$_2$SiP(Si*i*Pr$_3$)OC(Ph)=C(Ph)O (26), Is$_2$SiP(Si*i*Pr$_3$)C(Ph)(COPh)O (27), and Is$_2$SiP(Si*i*Pr$_3$)-1-O-3,5-C$_6$H$_2$(*t*Bu)$_2$-2-O (28). 26, 27: A solution of 300 mg (0.48 mmol) of **2a** in 20 mL of toluene was reacted with 100.8 mg (0.48 mmol) of PhC(O)C(O)Ph at −80 °C. The resulted colorless solution was slowly warmed to room temperature. At this stage, a mixture of **26** and **27** (1:9) was formed, from which the compound **26** could not be isolated. Therefore, **26** was characterized only by ^{31}P NMR spectroscopy (δ 116.3 (s)). Upon heating of this mixture at 110 °C for 3 h, the intermediate **26** was completely transformed into **27**. The latter was isolated by crystallization from 1 mL of hexane: Yield 312 mg (0.38 mmol, 78%) of a colorless solid: fp 177 °C; ^{1}H NMR (C_6D_6, 300 K) δ 0.39 (d, 3 H, CH*Me*$_2$, *J*(H,H) = 6.1 Hz), 0.56 (d, 3 H, CH*Me*$_2$, *J*(H,H) = 6.4 Hz), 0.72 (d, 3 H, CH*Me*$_2$, *J*(H,H) = 6.4 Hz), 0.97 (d, 3 H, CH*Me*$_2$, *J*(H,H) = 6.8 Hz), 1.03−1.32 (m, 39 H, CH*Me*$_2$), 1.52 (d, 3 H, CH*Me*$_2$, *J*(H,H) = 6.5 Hz), 1.78 (sept, 3 H, SiC*H*Me$_2$, *J*(H,H) = 7.5 Hz), 2.60 (sept, 1 H, *p*-C*H*Me$_2$, *J*(H,H) = 6.9 Hz), 2.74 (sept, 1 H, *p*-C*H*Me$_2$, *J*(H,H) = 6.9 Hz), 2.94 (sept, 1 H, *o*-C*H*Me$_2$, *J*(H,H) = 6.1 Hz), 3.41 (sept, 1H, *o*-C*H*Me$_2$, *J*(H,H) = 6.4 Hz), 4.02 (sept, 1 H, *o*-C*H*Me$_2$, *J*(H,H) = 6.5 Hz), 4.52 (sept, 1 H, *o*-C*H*Me$_2$, *J*(H,H) = 6.5 Hz), 6.65−8.16 (m, 14 H, arom H); ^{31}P NMR (C_6D_6, 300 K) δ −32.9 (s); ^{29}Si NMR (C_6D_6) δ 9.9 (d, Si*i*Pr$_3$, ^1J(Si,P) = 7 Hz), 1.3 (d, IsSi, ^1J(Si,P) = 4 Hz); selected ^{13}C{^{1}H} NMR (C_6D_6) data δ 92.95 (d, P−C, ^1J(C,P) = 23.3 Hz), 198.21 (s, C=O); IR (ν(CO)) 1642 cm^{-1}; EI-MS (*m/z* (%)) 833 (36) [M$^+$], 645 (38) [(M − Si*i*Pr$_3$)$^+$], 434 (58) [(Is$_2$SiH)$^+$], 105 (100) [PhCO$^+$]. Calcd for $C_{53}H_{77}O_2PSi_2$: C, 76.38; H, 9.31; P, 3.71; Found: C, 76.10; H, 9.29; P, 3.80.

28. A solution of 312 mg (0.5 mmol) of **2a** in 10 mL of toluene was treated with 110 mg (0.5 mmol) of 3,5-di-*tert*-butyl-*o*-benzoquinone at −78 °C. During the addition, the intense color of the quinone disappeared immediately and a colorless solution was formed after warming to room temperature. Removal of the solvent in vacuum (10^{-2} Torr) and crystallization of the residue from a little hexane at −78 °C afforded a colorless solid: Yield 400 mg (0.47 mmol, 94%); fp 191−192 °C; ^{31}P NMR (C_6D_6, 300 K) δ 114.3 (s); ^{29}Si NMR (C_6D_6) δ 16.6 (d, Si*i*Pr$_3$, ^1J(Si,P) = 53.1 Hz), −8.6 (d, IsSi, ^1J(Si,P) = 69 Hz); EI-MS (*m/z* (%)) 842 (81) [M$^+$], 685 (86) [(M − Si*i*Pr$_3$)$^+$], 628 (30) [(M − Si*i*Pr$_3$ − C_4H_9)$^+$], 57 (100) [$C_4H_9^+$]. Calcd for $C_{53}H_{87}O_2PSi_2$: C, 75.47; H, 10.39; P, 3.67. Found: C, 76.00; H, 10.41; P, 3.48.

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(34) Watanabe, H.; Takeuchi, K.; Nakajima, K.; Nagai, Y.; Goto, M. *Chem. Lett.* **1988**, 1343.

Table 7. Crystallographic Data for 1h, 20, 23, and 29

	1h	**20**	**23**	**29**
formula	$C_{42}H_{75}FGeLiO_2PSi$	$C_{50}H_{76}AsNSi_2$	$C_{52}H_{77}OPSi_2$	$C_{52}H_{77}AsN_2Si_2$
fw	769.6	822.2	805.3	861.3
cryst size ($mm^{3)}$)	0.6 × 0.7 × 0.7	0.3 × 0.5 × 0.5	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.6
a (Å)	12.933(7)	10.485(6)	34.305(9)	13.086(7)
b (Å)	17.473(12)	12.411(7)	16.141(4)	18.033(9)
c (Å)	21.277(16)	20.173(10)	17.767(9)	21.616(11)
α (deg)	90	100.99(4)	90	90
β (deg)	102.53(5)	97.20(4)	91.53(3)	95.86(3)
γ (deg)	90	100.99(4)	90	90
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
vol ($Å^{3)}$)	4694	2494	9834	5074
D_{calcd} ($g\ cm^{-3)}$)	1.09	1.10	1.09	1.13
Z	4	2	8	4
temp (°C)	−65	+20	−50	+20
abs coeff, μ ($cm^{-1)}$)	7.5	7.6	1.4	7.5
no. of reflecns measd	6411	7840	10 768	4968
no. of unique reflecns	6395	7840	10 542	4968
no. of observed reflecns	4881	4322	7615	2506
no. of params	510	508	1051	539
θ_{max} (deg)	23	24.5	21	22.5
h,k,l index range	−14/+12, 0/+19, 0/+23	−12/+11, −14/+13, 0/+22	0/+34, −16/0, −17/+17	−14/+7, 0/+18, 0/+22
$R1$ (%)[a]	3.9	6.8	5.4	6.8
w$R2$ (%)[a]	9.2	17.9	15.8	16.9

[a] $R1 = (\Sigma(|F_o| - |F_c|)/\Sigma|F_c|)$ for observed reflections. [b] $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2]^2)/\Sigma(w(F_o{}^2)^2\}^{1/2}$ for reflections measured.

Synthesis of $Is_2SiAs(Si\textit{i}Pr_3)N(N{=}CPh_2)$ (29). A solution of 860 mg (1.29 mmol) of **4a** in 20 mL of toluene was treated with 250.3 mg (1.29 mmol) of Ph_2CN_2 at −80 °C, leading to a yellow reaction mixture. The solution was allowed to warm to room temperature, the solvent was removed in vacuum (10^{-2} Torr), and the residue was taken up in 5 mL of hexane. Crystallization at −30 °C afforded pale yellow crystals: Yield 512 mg (0.59 mmol, 43%); fp 174 °C (dec); ^{1}H NMR (C_6D_6, 300 K) δ 1.00−1.29 (m, 57 H, CH*Me*$_2$ and SiC*H**Me*$_2$), 2.78 (sept, 2 H, *p*-C*H*Me$_2$, J(H,H) = 6.9 Hz), 3.93 (sept, 1 H, *o*-C*H*Me$_2$, J(H,H) = 6.9 Hz), 4.20 (br, 3 H, *o*-C*H*Me$_2$), 6.99−7.13 (m, 8 H, arom H), 7.45−7.49 (m, 5 H, arom H); ^{29}Si NMR (C_6D_6, 300 K) δ 21.0 (s, Si*i*Pr$_3$), −81.6 (s, Is$_2$Si); EI-MS (*m/z* (%)) 860 (0.1) [M$^+$], 832 (8) [(M − N$_2$)$^+$], 675 (12) [(M − N$_2$ − Si*i*Pr$_3$)$^+$], 433 (100) [(s$_2$Si − 1H)$^+$]; HRMS calcd for $C_{52}H_{77}AsN_2Si_2$ *m/z* 860.4820, found *m/z* 860.4814.

Thermolysis of $Is_2SiAs(Si\textit{i}Pr_3)N(N{=}CPh_2)$ (29). The compound, dissolved in toluene, was heated at 90 °C for 2 d in a sealed NMR tube, and the thermolysis was monitored by ^{29}Si NMR spectroscopy. The composition of the products Is$_2$SiPN=NCPh$_2$ (**30**) and Is$_2$SiPCPh$_2$ (**31**) were confirmed. **30**: HRMS calcd for $C_{52}H_{77}AsN_2Si_2$ *m/z* 860.4820, found *m/z* 860.4817. **31**: HRMS calcd for $C_{52}H_{77}AsSi_2$ *m/z* 832.4760, found *m/z* 832.4755.

Synthesis of $Is_2SiP(Si\textit{i}Pr_3)N(Mes)$ (33). 921 mg (1.48 mmol) amount of **2a** in 30 mL of toluene was reacted with 238 mg (1.48 mmol) of mesityl azide at −80 °C. The red reaction mixture was slowly warmed to room temperature and, subsequently, heated at 60 °C for 5 h to afford a clear yellow solution. Removal of the solvent in vacuum (10^{-2} Torr) leads to a yellow solid: Yield 1.16 g (1.48 mmol, 100%); fp 142−143 °C; ^{1}H NMR (C_6D_6, 300 K) δ 1.12−1.32 (m, 54 H, CH*Me*$_2$ and SiCH*Me*$_2$), 1.51 (sept, 3 H, SiC*H*Me$_2$, J(H,H) = 6.5 Hz), 2.10 (s, 3 H, *p*-Me), 2.62 (s, 6 H, *o*-Me), 2.78 (sept, 1 H, *p*-C*H*Me$_2$, J(H,H) = 6.9 Hz), 4.72 (br, 2 H, *o*-C*H*Me$_2$), 4.79 (s, 3 H, *o*-Me), 6.95 (s, 2 H, arom H), 7.19 (s, 4 H, arom H); ^{31}P NMR (C_6D_6, 300 K) δ −56.5 (s); ^{29}Si NMR (C_6D_6) δ 11.9 (d, Si*i*Pr$_3$, ^1J(Si,P) = 114.2 Hz), −64.7 (d, IsSi, ^1J(Si,P) = 38.4 Hz); EI-MS (*m/z* (%)) 755 (24) [M$^+$], 598 (40) [(M − Si*i*Pr$_3$)$^+$], 435 (58) [(Is$_2$SiH)$^+$]; HRMS calcd for $C_{48}H_{78}NPSi_2$ *m/z* 755.5386, found *m/z* 755.5388.

Synthesis of $Is_2SiC({=}NMes)N(Mes)C({=}PSi\textit{i}Pr_3)$ (34). A solution of **2a** (280 mg, 0.45 mmol) in 30 mL of toluene was treated with 130.5 mg (0.9 mmol) of mesityl isocyanide at −80 °C. The reaction mixture was allowed to warm to room temperature within 3 h, and subsequently, the solvent was removed in vacuum (10^{-2} Torr) to afford a yellow solid: Yield 410.5 mg (0.45 mmol, 100%); fp 212−213 °C (dec); ^{1}H NMR (C_6D_6, 300 K) δ 1.16−1.39 (m, 54 H, CH*Me*$_2$ and SiCH*Me*$_2$), 1.41 (d sept, 3 H, SiC*H*Me$_2$, J(H,H) = 6.5 Hz, ^3J(P,H) = 12 Hz), 2.11 (s, 3 H, *p*-Me), 2.18 (s, 3 H, *p*-Me), 2.29 (s, 6 H, *o*-Me), 2.32 (br, 6 H, *o*-Me), 2.78 (sept, 1 H, *p*-C*H*Me$_2$, J(H,H) = 6.9 Hz), 3.51 (br, 2 H, *o*-C*H*Me$_2$), 3.58 (br, 2 H, *o*-C*H*Me$_2$), 6.62 (s, 2 H, arom H), 6.75 (br, 2 H, arom H), 7.23 (s, 4 H, arom H); ^{31}P NMR (C_6D_6, 300 K) δ 93.5 (s); ^{29}Si NMR (C_6D_6) δ 10.2 (d, Si*i*Pr$_3$, ^1J(Si,P) = 95.8 Hz), −0.7 (d, IsSi, ^1J(Si,P) = 53.6 Hz); selected ^{13}C{^{1}H} NMR data δ 207.15 (d, C=P, ^1J(C,P) = 113.6 Hz), 169.40 (d, C=N, ^3J(C,P) = 14.5 Hz); IR (ν, cm^{-1}) 1643 (C=N), 1192 (C=P); EI-MS (*m/z* (%)) 908 (2) [M$^+$], 751 (46) [(M − Si*i*Pr$_3$)$^+$], 708 (81) [(M − Si*i*Pr$_3$ − C$_3$H$_7$)$^+$] 435 (100) [(Is$_2$SiH)$^+$], 119 (100) [Mes$^+$]; HRMS calcd for $C_{59}H_{89}N_2PSi_2$ *m/z* 908.6277, found *m/z* 908.6283.

Crystal Structure Determinations. Intensity data for **1h**, **20**, and **29** were collected on a Siemens-Stoe AED 2 and for **23** on a Syntex R3 diffractometer (Mo$_{K\alpha}$ radiation, λ = 0.7107 Å, ω-scan) and corrected for absorption (ψ-scans). The structures were solved by direct methods (SHELXS 86) and refined by using full-matrix least-squares techniques based on F^2 with all measured reflections (SHELXL 93).[35] Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were included in calculated positions, but only common isotropic temperature factors for equal hydrogen atoms were refined. The H atom at germanium in **1h** was located in the difference Fourier map and refined. Details of data collection and refinement are given in Table 7.

Acknowledgment. Support from the Deutsche Forschungsgemeinschaft (SFB 247), the Fonds der Chemischen Industrie, and Messer-Griesheim GmbH is gratefully acknowledged.

Supporting Information Available: Listings of atomic coordinates and *U* values, bonding parameters, and anisotropic displacement parameters for **1h**, **20**, **23**, and **29** (25 pages). Ordering information is given on any current masthead page.

OM9508851

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